

Appl. No. 10/811,414
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Marked up Version of Substitute Specification

SPECIFICATION

METHOD FOR MAKING A CARBON NANOTUBE BASED FIELD EMISSION DISPLAY METHOD FOR MAKING FIELD EMISSION DISPLAY

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a method for making a field emission display device, and more particularly to a method for making a carbon nanotube field emission display device. The present invention relates to a method for making a field emission display, and particularly to a method for making a carbon nanotube based field emission display.

2. Description of Prior Art

[0002] Carbon nanotubes are a novel carbonaceous material discovered by Iijima, a researcher of NEC corporation, in 1991. Relevant information was reported in an article by Iijima, entitled "Helical Microtubules of Graphitic Carbon" (Nature, Vol.354, P56, 1991). Carbon nanotubes can transmit an extremely high electrical current and emit electrons easily at a very low voltage of less than 100 volts, which make it a very promising potential material for field emission applications. Carbon nanotubes are very small tube-shaped structures having the composition of a graphite sheet rolled into a tube. Carbon nanotubes produced by arc discharge between graphite rods were first discovered and reported in an article by Sumio Iijima entitled "Helical Microtubules of Graphitic Carbon" (Nature, Vol. 354, Nov. 7, 1991, pp. 56-58). Carbon nanotubes have electrical conductance related to their structure, are chemically stable, and can have

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very small diameters (less than 100 nanometers) and large aspect ratios (length/diameter). Due to these and other properties, it has been suggested that carbon nanotubes can play an important role in field emission display devices.

[0003] Referring to FIG. 13, U.S. Pat. No. 6,232,706, invented by Hongjie Dai et al., discloses a field emission device using aligned parallel bundles of carbon nanotubes 100 extending from patterned catalyst layers 130 deposited on a layer of porous silicon 120 which is formed on a substrate 110 using a chemical vapor deposition (CVD) process. The carbon nanotubes produced by the CVD process have a variety of heights in a wide range so that the bundles of carbon nanotubes each forms a top which may be flat, concave, or in different pattern since the grown height is neither predictable nor controllable. Furthermore, a thin layer is formed on the top of the bundle which includes nanotubes with a variety of sizes, a number of remaining catalyst particles and amorphous carbon. These defects usually result in uniformity and unreliability of the field emission from the bundles of carbon nanotubes. US Pat. No. 6,339,281 discloses a method for making a triode-structure carbon nanotube based field emission display. The method comprises the steps of:

(1) forming a cathode electrode, a gate insulation layer and a gate electrode in sequence on a glass substrate;

(2) forming a gate opening in the gate electrode;

(3) forming a micro-cavity in the gate insulation layer; and

(4) forming a catalyst layer on the cathode electrode within the micro-cavity; and growing carbon nanotubes on the catalyst layer by chemical vapor deposition.

[0004] In order to optimize electron emissions, a triode-type field emission device is used. U.S. Pat. No. 6,515,415 discloses a typical

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~~triode type field emission device, which generally includes a cathode electrode having carbon nanotube array emitters, an anode electrode with a phosphor screen, and a gate electrode positioned between the cathode electrode and the anode electrode to control emission of electrons from the carbon nanotube array emitters. The carbon nanotube arrays are usually produced using a chemical vapor deposition process. However, in practice, there are the following persistent problems in fabricating carbon nanotube based field emission displays by chemical vapor deposition:~~

1. In order to achieve a uniform illuminance, a distance between gate electrodes and carbon nanotubes should be kept uniformly constant over a large area. However, it is difficult to assure a desired uniformity of heights of the carbon nanotubes over a large area by chemical vapor deposition.

2. In order to lower a threshold voltage of the gate electrodes, the distance between the gate electrodes and the carbon nanotubes should be as little as possible. However, it is difficult to precisely control a height of the carbon nanotubes to a micro-scale level by chemical vapor deposition.

3. A carbon nanotube array formed by chemical vapor deposition invariably contains a layer of randomly distributed carbon nanotubes, catalyst particles and a tiny amount of amorphous carbon, which impairs field emission performance of the carbon nanotube arrays and reduces the field emission display's product life cycle.

SUMMARY OF THE INVENTION

[0005] ~~In order to lower the emission turn on voltage, a precisely controlled distance between the emitters and the gate electrode is required. Although the carbon nanotubes array growth higher with longer the reaction time, it is very difficult to control the growth height precisely. Therefore, the distance between the emitters and the gate electrodes is~~

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~~difficult to control merely by growth. In order to resolve the above-mentioned problems, a method according to the present invention for making a carbon nanotube based field emission display comprises the steps of:~~

- (1) providing a detachable substrate having a plane surface;
- (2) forming gate electrodes in a predetermined pattern on the plane surface of the detachable substrate;
- (3) forming an intermediate layer on the gate electrodes;
- (4) forming a catalyst layer on the intermediate layer;
- (5) forming a spacer in a manner corresponding to a predetermined pattern on the layer of catalyst material;
- (6) forming carbon nanotube arrays extending from the layer of catalyst material;
- (7) forming cathode electrodes on first ends of the carbon nanotube arrays; and
- (8) removing the detachable substrate, and removing portions of the intermediate layer corresponding to positions of the carbon nanotube arrays so as to expose opposite second ends of the carbon nanotube arrays that face toward the gate electrodes.

SUMMARY OF THE INVENTION

[0006] ~~Accordingly, an object of the present invention is to provide a method for making a carbon nanotube-based field emission display device wherein a distance between emission tips and gate electrodes is precisely controllable. These and other features, aspects and advantages of the invention will become more apparent from the following detailed description, claims and the accompanying drawings, in which:~~

BRIEF DESCRIPTION OF THE DRAWINGS

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[0007] ~~In order to achieve the object set above, a method for making a carbon nanotube based field emission display device in accordance with a preferred embodiment of the invention comprises the following steps: providing an insulative layer having a first surface; depositing a layer of catalyst on the first surface of the insulative layer; forming a spacer having a plurality of openings therein such that patterned areas of the layer of catalyst are exposed; forming arrays of carbon nanotubes extending from the layer of catalyst in the openings of the spacer; forming a cathode electrode on a top of each of the arrays of carbon nanotubes; forming gate electrodes on a second, opposite surface of the insulative layer offset from the patterned areas; removing portions of the insulative layer corresponding to the arrays of carbon nanotubes so as to expose the arrays of carbon nanotubes; and attaching an anode electrode having a phosphor screen to the above obtained structure. A flatness of the first surface of the insulative layer is less than 1 micron so that the arrays of carbon nanotubes grown therefrom have a same flatness. A thickness of the insulative layer can be controlled through a deposition process so that a distance between the arrays of carbon nanotubes and the gate electrodes is controllable. Preferably, the thickness of the insulative layer is in the range from 1 micron to 1000 microns.~~ FIG. 1 is a schematic side elevation view of a detachable substrate used in a preferred method for making a field emission field display in accordance with the present invention;

[0008] ~~Other objects, advantages and novel features of the present invention will become more apparent from the following detailed description when taken in conjunction with the accompanying drawings, in which:~~ FIG. 2 is similar to FIG. 1, but showing gate electrodes formed on a first protective layer of the detachable substrate;

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] ~~FIG. 1 is a flow chart of a method for making a carbon~~

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~~nanotube-based field emission display device in accordance with a preferred embodiment of the invention; FIG. 3 is similar to FIG. 2, but showing an intermediate layer formed on the gate electrodes;~~

[0010] ~~FIG. 2 is a schematic, side elevation view of a working plate having a number of grooves of small size therein; FIG. 4 is similar to FIG. 3, but showing a second protective layer formed on the intermediate layer;~~

[0011] ~~FIG. 3 is a schematic, side elevation view of an insulative layer deposited on the working plate of FIG. 1; FIG. 5 is similar to FIG. 4, but showing a catalyst layer formed on the first protective layer;~~

[0012] ~~FIG. 4 is a schematic, side elevation view of a protective layer deposited on the insulative layer of FIG. 3; FIG. 6 is similar to FIG. 5, but showing a spacer formed on the catalyst layer;~~

[0013] ~~FIG. 5 is a schematic, side elevation view of a layer of catalyst deposited on the protective layer of FIG. 4; FIG. 7 is similar to FIG. 6, but showing carbon nanotube arrays formed on the catalyst layer of FIG. 6;~~

[0014] ~~FIG. 6 is a schematic, side elevation view of arrays of carbon nanotubes grown from the catalyst within a plurality of perforations of a barrier formed on the layer of catalyst of FIG. 5; FIG. 8 is similar to FIG. 7, but showing a layer of negative feedback resistance formed on tops of the carbon nanotube arrays;~~

[0015] ~~FIG. 7 is a schematic, side elevation view of a plurality of resistive negative feedback layers formed on the corresponding arrays of carbon nanotubes of FIG. 6; FIG. 9 is similar to FIG. 8, but showing cathode electrodes formed on the layer of negative feedback resistance;~~

[0016] ~~FIG. 8 is a schematic, side elevation view of a plurality of cathode electrodes formed on the corresponding resistive negative feedback layers of FIG. 7; FIG. 10 is similar to FIG. 9, but showing the cathode electrodes packaged with a cover;~~

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[0017] ~~FIG. 9 is a schematic, side elevation view of a base coupled with the cathode electrodes and the barrier of FIG. 8; FIG. 11 is similar to FIG. 10, but showing the subassembly thereof inverted, with the detachable substrate removed, and unwanted portions of the first protective layer and the intermediate layer removed;~~

[0018] ~~FIG. 10 is a schematic, side elevation view of a number of gate electrodes formed on a second surface opposite to the first surface of the insulative layer after removal of the working plate of FIG. 9; FIG. 12 is similar to FIG. 11, but showing unwanted portions of the second protective layer removed; and~~

[0019] ~~FIG. 11 is a schematic, side elevation view of the assembly of FIG. 10 after removing portions of the insulative layer, the protective layer, and the layer of catalyst; FIG. 13 is a similar to FIG. 12, but showing the subassembly thereof assembled with a display screen to obtain a field emission display.~~

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0020] ~~FIG. 12 is a schematic, side elevation view of a carbon nanotube based field emission display device made by adding a phosphor screen to the device of FIG. 11; and Reference will now be made to the drawings to describe the preferred method of the present invention in detail.~~

[0021] ~~FIG. 13 is a schematic view of a conventional carbon nanotube field emission device. Referring to FIG. 13, a field emission display produced by the preferred method of the present invention comprises: cathode electrodes 17, an anode electrode 20, gate electrodes 19 arranged between the cathode electrodes 17 and the anode electrode 20, carbon nanotube arrays 15, and a spacer 14. A layer of negative feedback~~

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resistance 16 is formed between first ends of the carbon nanotube arrays 15 and the cathode electrodes 17. Opposite second ends of the carbon nanotube arrays 15 are flush with corresponding ends of the spacer 14 that are nearest the gate electrodes 19. The cathode electrodes 17 are packaged with a bottom cover 18.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

[0022] A preferred method for making a carbon nanotube-based field emission display device in accordance with the invention will be described below with reference to FIG. 1. Referring to FIG. 1, a detachable substrate 10 having a flat surface (not labeled) is first provided. Preferably, a plurality of grooves or apertures 101 is defined in the surface of the detachable substrate 10, for facilitating removal of the detachable substrate 10 in a later step. The surface is preferably coated with a removable material such as wax, so as to achieve a variation in flatness of the surface of less than 1μm. The detachable substrate 10 is generally made of refractory material which is capable of resisting high temperatures. A first protective layer (not shown) is then formed on the surface of the detachable substrate 10. The first protective layer is for protecting the gate electrodes 17 from being obstructed by carbonaceous materials that are generally by-products of formation of the carbon nanotube arrays 15 in a later step. Generally, the first protective layer comprises material selected from the group consisting of glass, silicon, silicon oxide, mica, and ceramic material. The first protective layer has a thickness in the range from 10nm~10μm. It should be noted that formation of the first protective layer is not an essential step in practicing the present invention.

[0023] Step 1 is providing a working plate. This is an optional step for the purpose of conveniently carrying out the subsequent steps. The working plate can be a nonmetallic material or a metallic material that is sufficiently

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~~heat stable to endure high temperatures at which carbon nanotubes are produced.~~ Referring to FIG. 2, the gate electrodes 19 are formed on the first protective layer in a predetermined pattern. The gate electrodes 19 can be formed by e-beam evaporation, thermal evaporation or sputtering, each of these methods being performed in cooperation with either a mask or photolithography. The gate electrodes 19 can be made of metallic material. The metallic material is preferably capable of withstanding temperatures of about 700°C, and preferably has a coefficient of thermal expansion compatible with those of the first protective layer, an intermediate layer 11 (see FIG. 3), a second protective layer 12 (see FIG. 4), and the spacer 14.

[0024] Step 3 is forming an insulative layer on the working plate. The insulative layer is made of insulative material such as silicon oxide, and has a predetermined thickness. In order to form carbon nanotubes from a common surface, a first surface of the insulative layer should be smooth and flat. Preferably, a variation in flatness of the first surface is less than 1 micron. Referring to FIG. 3, the intermediate layer 11 is formed on the gate electrodes 19 by coating or printing. The intermediate layer 11 may alternatively be substituted by a thin plate. The intermediate layer 11 is for controlling a distance between the carbon nanotube arrays 15 and the gate electrodes 19, and is also used as a substrate for growing of the carbon nanotube arrays 15 in the later step. A thickness of the intermediate layer 11 is in the range from 1μm to 1000μm, and preferably in the range from 10μm to 200μm. A variation in flatness of the intermediate layer 11 is preferably controlled to be less than 1μm. The intermediate layer 11 is generally made of material which is capable of being processed by photolithography and enduring temperatures of about 700°C. Accordingly, the intermediate layer 11 generally comprises material selected from the group consisting of glass, silicon, silicon oxide, mica, and ceramic material.

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[0025] ~~Step 3 is depositing a layer of catalyst on the first surface of the insulative layer. Generally, the catalyst is a transition metal such as Fe (Iron), Co (Cobalt), Ni (Nickel), or an alloy thereof. A thickness of the layer of catalyst is in the range from 1nm to 10nm, and preferably in the range from 3nm to 5nm. Further, the layer of catalyst is preferably annealed at a temperature of 300 degree-400 degree. Referring to FIG. 4, preferably, a second protective layer 12 is deposited on the intermediate layer 11 by e-beam evaporation or sputtering. The second protective layer 12 is for protecting carbon nanotube arrays 15 from being damaged or destroyed during a later step of wet etching. Preferably, the second protective layer 12 is made of silicon. Alternatively, the second protective layer 12 can be made of another suitable material which is capable of withstanding a wet etching process, and yet which is removable by a dry etching process. The second protective layer 12 is as thin as possible, and preferably in the range from 10nm to 1μm. It should be noted that deposition of the second protective layer 12 is not an essential step in practicing the present invention.~~

[0026] ~~Step 4 is forming a barrier on the layer of catalyst. The barrier has a predetermined height according to a height of carbon nanotubes produced in the following step. The height of the barrier is generally in the range from 1 micron to 1000 microns, and preferably in the range from 10 microns to 500 microns. The barrier has a plurality of perforations (not labeled) so as to define a plurality of pixel areas within which carbon nanotubes can subsequently be grown. The material of the barrier should be a heat stable material that can endure the high temperatures at which carbon nanotubes grow. Such material can be heatproof glass, metal coated with insulative material, silicon, silicon oxide, ceramic material, or mica. Referring to FIG. 5, a catalyst layer 13 is deposited on the second protective layer 12 by e-beam evaporation, thermal evaporation or sputtering. The~~

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catalyst layer 13 can generally be iron, cobalt, nickel, or any suitable combination alloy thereof. A thickness of the catalyst layer 13 is in the range from 1nm to 10nm, and preferably about 5nm.

[0027] Step 5 is growing arrays of carbon nanotubes from the catalyst within the plurality of perforations of the barrier. A preferred chemical vapor deposition process for growing arrays of carbon nanotubes includes: heating carbon containing gas, such as ethylene or acetylene, to a temperature of about 700 degree, introducing the carbon containing gas to a reaction region having catalyst pattern, and producing arrays of carbon nanotubes on the catalyst. The reaction is stopped when the arrays of carbon nanotubes have reached or just exceeded the height of the barrier. Referring to FIG. 6, the spacer 14 having a predetermined pattern is formed on the catalyst layer 13 by coating or printing. The spacer 14 is for insulating the gate electrodes 19 from the cathode electrodes 17, and for defining spaces 141 for growing the carbon nanotube arrays 15. The spacer 14 may alternatively be substituted by a thin plate. A surface of the thin plate which is attached to the catalyst layer 13 preferably has a variation in flatness of less than 1μm. A thickness of the spacer 14 is related to and determined by heights of the carbon nanotube arrays 15. Generally, the thickness of the spacer 14 is in the range from 1μm to 1mm, and preferably in the range from 10μm to 500μm. The spacer 14 is made of material which is capable of enduring temperatures of about 700°C. Accordingly, the spacer 14 generally comprises material selected from the group consisting of glass, metal coated insulating material, silicon oxide, mica, and ceramic material. [0028] Step 6 is forming a cathode electrode on a top of each of the arrays of carbon nanotubes. Generally, the forming of cathode electrodes employs a coating process or chemical deposition of metallic material. Referring to FIG. 7, the carbon nanotube arrays 15 are formed in the spaces 141 defined by the spacer 14 by

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conventional chemical vapor deposition. The heights of the carbon nanotube arrays 15 are controlled to be approximately equal to the thickness of the spacer 14.

[0029] Step 7 is forming a base and removing the working plate. The base is made of insulative material, such as glass, plastic, or ceramic material. The base has an inner configuration complementary with an outer configuration of the cathode electrodes and the barrier, so that the base can be coupled thereto. After removing the working plate, a second surface of the insulative layer is exposed. Referring to FIG. 8, the layer of negative feedback resistance 16 is then formed for the purposes of associated driving circuits. The layer of negative feedback resistance 16 is generally deposited on the carbon nanotube arrays 15 by e-beam evaporation, thermal evaporation or sputtering. The layer of negative feedback resistance 16 can be made of silicon or an oxide of silicon.

[0030] Step 8 is forming gate electrodes on the exposed second surface of the insulative layer according to the pixel areas. Referring to FIG. 9, the cathode electrodes 17 are formed on the layer of negative feedback resistance 16. The cathode electrodes 17 can be formed by e-beam evaporation, thermal evaporation or sputtering. The cathode electrodes 17 can be made of metallic material. A coefficient of thermal expansion of the metallic material is preferably compatible with those of the first protective layer, the intermediate layer 11, the second protective layer 12, the spacer 14, and the bottom cover 18.

[0031] Step 9 is removing portions of the insulative layer corresponding to the pixel areas so as to expose the arrays of carbon nanotubes. Electrons emitting from the arrays of nanotubes can thereby pass out from the assembly. A further recommended step is to treat the exposed surfaces of the arrays of carbon nanotubes with a laser to clean the surfaces and improve the uniformity of electron emissions therefrom.

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Referring to FIG. 10, the cathode electrodes 17 are packaged with a bottom cover 18 by printing, fusion or a suitable bonding method. The bottom cover 18 can be made of glass, plastic, or ceramic material.

[0032] ~~Step 10 is packaging a phosphor screen with an anode electrode onto the assembly to form the assembled carbon nanotube field emission display device. Referring to FIG. 11, the detachable substrate 10 is removed, and portions of the first protective layer and intermediate layer 11 are removed by a wet etching process. Said portions correspond to positions of the carbon nanotube arrays 15.~~

[0033] ~~It is to be understood that the exposed surfaces of the arrays of carbon nanotubes have a same flatness as the first surface of the insulative layer. Further, that a distance between the arrays of carbon nanotubes and the gate electrodes is determined by a thickness of the insulative layer, because a thickness of the layer of catalyst is negligible compared with that of the insulative layer. Accordingly, said distance is precisely controllable through regulation of the deposition of the insulative layer. Referring to FIG. 12, portions of the second protective layer 12 are removed by a dry etching process. Said portions correspond to the positions of the carbon nanotube arrays 15. A laser is applied to remove corresponding portions of the catalyst layer 13, in order to expose the second ends of the carbon nanotube arrays 15 to the gate electrodes 19. Preferably, the laser is also applied to the second ends of the carbon nanotube arrays 15 themselves, to clean said second ends.~~

[0034] ~~Referring to FIGS. 2 through 12, each step of the preferred method is described in more detailed below: Referring to FIG. 13, a display screen is provided. The display screen comprises a glass substrate 21 with the anode electrode 20 formed thereon, and phosphor layers 22 formed on the anode electrode 20. The display screen is attached to the subassembly obtained in step 12.~~

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[0035] Referring to FIG. 2, a working plate 20 is provided with a plurality of grooves (not labeled) define therein, the grooves facilitating subsequent removal of the working plate 20. In order to flatten the surface of the working plate 20, the grooves can be filled with an easily removable material such as wax (not shown). While the present invention has been described with reference to particular embodiments, the description is illustrative of the invention and is not to be construed as limiting the invention. Therefore, various modifications can be made to the described embodiments by those skilled in the art without departing from the true spirit and scope of the invention as defined by the appended claims.

[0036] Referring to FIG. 3, a silicon oxide layer 22 is deposited on the working plate 20. The silicon oxide layer 22 has a first surface, and is removable by a wet etching process. Preferably, a variation in flatness of the first surface is less than 1 micron. A thickness of the silicon oxide layer 22 is precisely controllable through the deposition process. The thickness is generally in the range from 1 micron to 1000 microns, and preferably in the range from 10 microns to 200 microns.

[0037] Referring to FIG. 4, a protective layer 24 is deposited on the silicon oxide layer 22. The protective layer 24 is made of silicon, which can endure wet etching and is removable by a dry etching process. A thickness of the protective layer 24 is in the range from 10 nm to 100 nm.

[0038] Referring to FIG. 5, a layer of catalyst 26 is deposited with a thickness from 1nm to 10nm on the protective layer 24. The catalyst is made of Fe, Co, Ni, or an alloy thereof.

[0039] Referring to FIG. 6, a barrier 28 is formed with a plurality of perforations (not labeled), and carbon nanotube arrays 30 are grown from the layer of catalyst 26 within the perforations. The barrier 28 is made of insulative material, and has a predetermined height in the range from 10 microns to 500 microns. The carbon nanotube arrays 30 are produced by a

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~~chemical vapor deposition process, and heights of the arrays 30 are approximately equal to a height of the barrier 28.~~

[0040] Referring to FIG. 7, a negative feedback layer 32 is formed on a top of each of the carbon nanotube arrays 30, so that the carbon nanotube arrays 30 electrically contact the negative feedback layers 32. The negative feedback layers 32 are made of a material having a suitable resistance, such as silicon or alloys.

[0041] Referring to FIG. 8, a cathode electrode 34 is formed on each negative feedback layer 32. The cathode electrodes 34 are made of metallic material having a heat expansion coefficient compatible with that of the negative feedback layers 32.

[0042] Referring to FIG. 9, a base 36 is formed on the cathode electrodes 34. The base 36 is made of insulative material, such as glass, plastic or ceramic material. The base 36 has an inner configuration complementary with an outer configuration of the cathode electrodes 34 and the barrier 28, so that the base 36 can be coupled thereto.

[0043] Referring to FIG. 10, the working plate 20 is removed to expose a second surface of the silicon oxide layer 22. Gate electrodes 40 are then deposited on the second surface offset from the positions of the carbon nanotube arrays 30.

[0044] Referring to FIG. 11, portions of the silicon oxide layer 22 and the protective layer 24 are removed by a wet etching process and a dry etching process respectively. Consequently, the carbon nanotube arrays 30 are exposed. Furthermore, if considered necessary, the carbon nanotube arrays 30 are exposed to laser irradiation in order to clean the surfaces thereof.

[0045] Referring to FIG. 12, an anode electrode 50 having a phosphor layer 52 is packaged onto the assembly, thereby providing the assembled